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(54) POLYMERIZATION-INHIBITING COMPOSITION, POLYMERIZATION INHIBITOR AND METHOD FOR INHIBITING POLYMERIZATION

(57) The invention relates to a polymerization inhibitor comprising at least one compound (a) selected from the group consisting of a compound having an NO radical in its molecule and a precursor compound capable of forming an NO radical, and a phosphorus-containing compound (b), wherein a weight ratio of the compound (a) to the phosphorus-containing compound (b) is 1:10 to 100:1.

Specifically, the invention provides a method for inhibiting the polymerization of at least one monomer (c) selected from the group consisting of a conjugated diene, an aromatic vinyl, an ethylenically unsaturated nitrile and an α-olefin, comprising causing the polymerization inhibitor to coexist with the monomer (c), and a polymerization-inhibiting composition comprising the polymerization inhibitor and the monomer (c).

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Description

TECHNICAL FIELD

[0001] The present invention relates to techniques for inhibiting the polymerization of a monomer such as a conjugated diene, aromatic vinyl, ethylenically unsaturated nitrile or α-olefin, and more particularly to a polymerization-inhibiting composition, a polymerization inhibitor and a polymerization-inhibiting method for inhibiting the occurrence of unfavorable premature polymerization in various operating steps such as the production, purification, storage, shipment, preparation and use of such a monomer, a mixture of the monomers or a hydrocarbon mixture containing the monomer.

BACKGROUND ART

[0002] A monomer such as a conjugated diene, aromatic vinyl, ethylenically unsaturated nitrile or α-olefin is easy to cause premature polymerization in various operating steps such as the production, purification, storage, shipment, preparation and use thereof. The occurrence of the premature polymerization causes contamination of the monomer with a polymer, increase of viscosity, gelling, loss in reactivity, etc. In addition, by the premature polymerization, a heat exchanger, storage container, transfer line, pump, distilling apparatus or the like is stained with the polymer, and so problems such as increase in the cost of washing, lowering in production efficiency and loss of material occur. The problems relating to such premature polymerization will be described more specifically taking the case of a purification step of a conjugated diene.

[0003] Conjugated dienes, conjugated diene-containing hydrocarbon mixtures (for example, C_4 hydrocarbon fraction and C_5 hydrocarbon fraction), conjugated diene-containing unsaturated olefin hydrocarbon mixtures (mixtures in a recovery step of olefin hydrocarbon compounds after gas and liquid cracking or decomposing processes), conjugated diene-containing monomer mixtures (for example, monomer mixtures for production of synthetic rubbers) and the like are easy to undergo polymerization of the conjugated dienes and/or copolymerization of the conjugated dienes with any other copolymerizable unsaturated compound upon distillation, extractive distillation, extraction, countercurrent extraction, hydrogenation or hydrotreating, hydrorefining, heat treatment, other similar treatments. preheating before treatment, storage, transfer or processing.

[0004] For example, when a purified conjugated diene is isolated and recovered from a conjugated diene-containing hydrocarbon mixture by a distillation process including extractive distillation, a polymerization reaction is easy to occur to form a solvent-soluble polymer or a crosslinked, solvent-insoluble polymer. The solvent-soluble polymer is called a rubbery polymer and stains various apparatus or devices such as an extractive distillation column, distillation column, heat exchanger and piping. The crosslinked, solvent-insoluble polymer is a porous insoluble polymer and is called a popcorn polymer due to its appearance. This popcorn polymer is particularly undesirable because not only it self-multiplies in the presence of the vapor or liquid of the conjugated diene to rapidly clog the apparatus, but it is extremely difficult to remove and control. Once the popcorn polymer is formed, it multiplies, so to speak, exponentially, in that it serves as a seed. Since the popcorn polymer is a strong crosslinked polymer, it is insoluble in any already-known solvent and not melted. Accordingly, in order to remove the popcorn polymer, there is no effective cleaning method, but it is cleaned out by a mechanical means. The cleaning of the apparatus requires to suspend and disjoint it so as to mechanically remove the deposit of the polymer, and so it takes time, and economical disadvantage is unavoidable. In addition, since the popcorn polymer cannot be completely removed by the mechanical cleaning, the popcorn polymer remaining in the apparatus in a trace amount serves as a seed to start the multiplication of the popcorn polymer again when the operation of the apparatus is resumed.

[0005] In a process of preparing a purified conjugated diene by subjecting a hydrocarbon mixture containing the conjugated diene to a distillation process including extractive distillation, conditions liable to induce a polymerization reaction, such as coexistence of a gas phase with a liquid phase, moderate operating temperature, high monomer purity, mixing of water and presence of iron rust, gather. Accordingly, there have heretofore been proposed methods making use of various kinds of polymerization inhibitors. However, in some cases, the insufficient polymerization inhibiting effects thereof may have made it difficult to prevent the formation of a rubbery polymer and/or a popcorn polymer, so that the apparatus is clogged. When the polymerization inhibitor is used in a large amount to enhance the polymerization inhibiting effect, there occur such problems that a tar-like product is formed to waste energy, and the extraction efficiency of the extractive distillation is lowered.

[0006] In a process of recovering an olefin hydrocarbon compound such as ethylene, propylene, butene, butadiene or a mixture thereof after gas and liquid cracking or decomposing processes, treatments such as an isolating process of various kinds of olefin hydrocarbon compounds are conducted by conversion by hydrogenation, distillation or extraction of olefin compounds and acetylene compounds. Deposit (scale) considered to be attributable to the polymerization of conjugated dienes and/or the like is easy to form on apparatus for these treatments. When such deposit is built up to

an excessive extent, thermal efficiency of the apparatus and isolation efficiency of a distillation column are lowered, and clogging of piping is caused. In addition, a monomer mixture containing a conjugated diene and a vinyl aromatic compound such as styrene has been known to show a tendency to polymerize during its storage.

[0007] There has heretofore been proposed a method of distilling a C_5 hydrocarbon fraction in the presence of N,N-dialkylhydroxylamine in order to inhibit the polymerization of a conjugated diene-containing petroleum fraction in a distillation apparatus (Japanese Patent Application Laid-Open No. 112304/1975). However, the mere use of N,N-dialkylhydroxylamine is not sufficient in the polymerization-inhibiting effect. U.S. Patent No. 3,371,124 has proposed a method of using N,N-dialkylhydroxylamine and the oxalate [bis(diethylhydroxylamine) oxalate] thereof as polymerization inhibitors in order to inhibit the formation of a popcorn polymer in a recovery system by fractional distillation of a monomer containing at least one conjugated diene discharged from a production process of SBR. The oxalate can be obtained by reacting N,N-dialkylydroxylamine with oxalic acid. However, oxalic acid involves a problem that it corrodes an extractive distillation column. The mere use of the oxalate is not sufficient in the polymerization-inhibiting effect.

[0008] Japanese Patent Application Laid-Open No. 189810/1992 discloses a method of causing [Group A] hydroquinone, hydroquinone monomethyl ether, p-methoxyphenyl, phenothiazine, piperidine, etc. and [Group B] phosphorus-containing compounds such as phosphoric acid and potassium phosphate to coexist with a molecular oxygen-containing gas in order to inhibit thermal polymerization upon epoxidation of a double bond in a cyclohexenyl ring by causing an epoxidizing agent to act on a mixture of (meth)acrylates having a cyclohexenyl group in their ester moieties. However, it has been found that when a combination of hydroquinone shown as a representative example of Group A in this publication with a phosphorus-containing compound in Group B is used to conduct extractive distillation of a conjugated diene-containing hydrocarbon mixture, a sufficient polymerization-inhibiting effect cannot be achieved.

[0009] Further, it has heretofore been proposed to use a compound having a stable NO radical (free radical) in its molecule or a compound forming a stable NO radical *in situ* under treating conditions as a polymerization inhibitor (Japanese Patent Application Laid-Open No. 26639/1992, etc.). However, the mere use of these compounds fails to achieve a sufficient polymerization-inhibiting effect.

[0010] Such problems of premature polymerization are easy to occur at various operating steps in not only conjugated dienes, but also many other monomers.

DISCLOSURE OF THE INVENTION

[0011] It is an object of the present invention to provide a polymerization inhibitor and a method of inhibiting polymerization for inhibiting the occurrence of unfavorable premature polymerization in various operating steps such as the production, purification, storage. shipment, preparation and use of a monomer such as a conjugated diene, aromatic vinyl, ethylenically unsaturated nitrile or α-olefin, a mixture of the monomers or a hydrocarbon mixture containing such a monomer.

[0012] Another object of the present invention is to provide a polymerization-inhibiting composition containing the monomer and polymerization inhibitor described above.

[0013] A particular object of the present invention is to provide a novel polymerization inhibitor, method of inhibiting polymerization and polymerization-inhibiting composition containing a conjugated diene and the polymerization inhibitor for inhibiting (co)polymerization of the conjugated diene upon the treatment, storage or the like of the conjugated diene, a conjugated diene-containing hydrocarbon mixture, a conjugated diene-containing unsaturated olefin hydrocarbon mixture, a conjugated diene-containing monomer mixture, or the like at a high level.

[0014] The present inventors have carried out an extensive investigation with a view toward overcoming the above-described problems involved in the prior art. As a result, it has been found that the combined use of at least one compound selected from the group consisting of a compound having an NO radical (NO•) in its molecule and a precursor compound capable of forming an NO radical and a phosphorus-containing compound as a polymerization inhibitor is extremely effective for the inhibition of premature polymerization of various kinds of monomers such as conjugated dienes.

[0015] The polymerization inhibitor according to the present invention can markedly inhibit the formation of a popcorn polymer and a rubbery polymer when it is caused to exist in a distillation step in a process for isolating and producing a purified conjugated diene by conducting a distillation process including extractive distillation from, for example, a conjugated diene-containing hydrocarbon mixture. The polymerization inhibitor according to the present invention is extremely effective for not only hydrocarbon mixtures and the like containing a conjugated diene in a great amount, but also hydrocarbon mixtures and the like containing a conjugated diene in a small amount. The polymerization inhibitor according to the present invention is also effective for the inhibition of polymerization of monomers such as aromatic vinyls, ethylenically unsaturated nitriles and α-olefins. The present invention has been led to completion on the basis of these findings.

[0016] According to the present invention, there is thus provided a polymerization-inhibiting composition comprising at least one compound (a) selected from the group consisting of a compound having an NO radical in its molecule

and a precursor compound capable of forming an NO radical, a phosphorus-containing compound (b), and at least one monomer (c) selected from the group consisting of a conjugated diene, an aromatic vinyl, an ethylenically unsaturated nitrile and an α-olefin, wherein a weight ratio of the compound (a) to the phosphorus-containing compound (b) is 1:10 to 100:1.

[0017] According to the present invention, there is also provided a polymerization inhibitor for at least one monomer (c) selected from the group consisting of a conjugated diene, an aromatic vinyl, an ethylenically unsaturated nitrile and an α-olefin, comprising at least one compound (a) selected from the group consisting of a compound having an NO radical in its molecule and a precursor compound capable of forming an NO radical, and a phosphorus-containing compound (b), wherein a weight ratio of the compound (a) to the phosphorus-containing compound (b) is 1:10 to 100:1.

[0018] According to the present invention, there is further provided a method for inhibiting polymerization, which comprises causing at least one compound (a) selected from the group consisting of a compound having an NO radical in its molecule and a precursor compound capable of forming an NO radical, and a phosphorus-containing compound (b) to coexist at a weight ratio of the compound (a) to the phosphorus-containing compound (b) of 1:10 to 100:1 with at least one monomer (c) selected from the group consisting of a conjugated diene, an aromatic vinyl, an ethylenically unsaturated nitrile and an α-olefin.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

Fig. 1 is a flow diagram illustrating a distillation process including an extractive distillation step for obtaining purified 1,3-butadiene from a C_4 hydrocarbon fraction.

BEST MODE FOR CARRYING OUT THE INVENTION

1. Monomer:

[0020] The polymerization-inhibiting technique according to the present invention can be applied to conjugated dienes, aromatic vinyls, ethylenically unsaturated nitriles and α-olefins. Examples of the conjugated dienes include 1,3-butadiene, isoprene, chloroprene and the like. Examples of the aromatic vinyls include styrene, vinyltoluene, α-methylstyrene and the like. Examples of the ethylenically unsaturated nitriles include acrylonitrile, methacrylonitrile and the like. Examples of the α-olefins include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene and the like.

[0021] Among others, the polymerization inhibitor according to the present invention is particularly effective for inhibiting the formation of a popcorn polymer and a rubbery polymer in a production process of a purified conjugated diene, comprising isolating the conjugated diene by conducting a distillation process including extractive distillation from a conjugated diene-containing hydrocarbon mixture. The conjugated dienes will hereinafter be described in detail.

2. Conjugated diene:

[0022] In the present invention, as the conjugated dienes, may be mentioned 1,3-butadiene, isoprene, chloroprene and the like. The polymerization inhibitor according to the present invention is suitable for conjugated dienes or conjugated diene-containing mixtures. As the conjugated diene-containing mixtures, may be mentioned conjugated diene-containing hydrocarbon mixtures, conjugated diene-containing unsaturated olefin hydrocarbon mixtures, conjugated diene-containing monomer mixtures and the like.

[0023] The conjugated diene-containing hydrocarbon mixture is a mixture of various kinds of hydrocarbons containing at least one conjugated diene. No particular limitation is imposed on a conjugated diene-containing hydrocarbon mixture used as a starting material for isolating and producing a purified conjugated diene. However, as representative examples thereof, may be mentioned petroleum fractions such as an isoprene-containing C_5 hydrocarbon fraction and a 1,3-butadiene-containing C_4 hydrocarbon fraction.

[0024] The C_5 hydrocarbon fraction is secondarily produced upon the production of ethylene by steam cracking or another high-temperature treatment of a hydrocarbon. The C_5 hydrocarbon fraction generally has a boiling point ranging from 25°C to 70°C and contains various kinds of C_5 hydrocarbons different in degree of saturation and may contain some C_4 hydrocarbons and C_6 hydrocarbons. The C_5 hydrocarbon fraction generally contains n-pentane, isopentane, 1-pentene, 2-methyl-1-butene, trans-2-pentene, cis-2-pentene, 2-methyl-2-butene, isoprene, trans-1,3-pentadiene, cis-1,3-pentadiene, 1,4-pentadiene, 2-butyne, isopropenylacetylene, isopropylacetylene, cyclopentane, cyclopentene, cyclopentadiene and the like.

[0025] The C_4 hydrocarbon fraction such as naphtha-cracked oil generally contains various kinds of hydrocarbons

such as propane, propylene, isobutene, allene, n-butane, isobutene, 1-butene, trans-2-butene, cis-2-butene, 1,3-butadiene, methylacetylene, 1,2-butadiene and vinylacetylene.

[0026] As the conjugated diene-containing unsaturated olefin hydrocarbon mixtures, may be mentioned unsaturated olefin hydrocarbon mixtures in a recovery step of olefin hydrocarbon compounds such as ethylene, propylene, butene, butadiene and mixtures thereof after gas and liquid cracking or decomposing processes. Ethylene, propylene, butene, butadiene and the like are isolated and recovered from these unsaturated olefin hydrocarbon mixtures by a process including hydrogenation, distillation, extraction and/or the like.

[0027] As examples of the conjugated diene-containing monomer mixtures, may be mentioned monomer mixtures for preparation of synthetic rubber such as SBR.

[0028] The polymerization inhibitor according to the present invention can be applied to conjugated diene-containing liquid mixtures in addition to the above-described mixtures.

3. Extractive distillation:

[0029] The polymerization inhibitor according to the present invention is particularly suitable for use in inhibiting the formation of a popcorn polymer and a rubbery polymer in an extractive distillation step in a process for isolating and producing a purified conjugated diene by conducting a distillation process including extractive distillation from a conjugated diene-containing hydrocarbon mixture. Therefore, the extractive distillation will hereinafter be described in detail.

[0030] As the distillation process including extractive distillation, a single extractive distillation process or a combination of plural extractive distillation processes may be only conducted. However, when a hydrocarbon mixture containing many kinds of hydrocarbons is used as a starting material, an extractive distillation step may also be combined with a distillation step (fractional distillation step) making good use of a difference between boiling points.

[0031] As an example of the distillation process including extractive distillation, may be mentioned a process for recovering high-purity isoprene from a C_5 hydrocarbon mixture described in Japanese Patent Application Laid-Open No. 41323/1972. More specifically, this publication describes a process for recovering high-purity isoprene, in which (1) a C_5 hydrocarbon mixture as a raw material is subjected to extractive distillation in the presence of an N-alkyl-substituted lower fatty acid amide solvent containing a polymerization inhibitor to remove hydrocarbons more hardly soluble than isoprene, (2) the thus-extracted isoprene and hydrocarbons more easily soluble than isoprene are then distilled to remove most of cyclopentadiene and hydrocarbons having a higher boiling point than isoprene, (3) the resultant fraction is subjected further to extractive distillation in the presence of the above-described solvent to remove the remaining cyclopentadiene and easily soluble hydrocarbons such as isopropenylacetylene, and (4) the solvent before circulating to the extractive distillation is subjected to a stripping treatment under such reduced pressure that the stripping temperature amounts to 140°C or lower. In the publication, a flow diagram of the recovery process is illustrated and quoted for reference in explanation of the present invention.

[0032] As an example of a process for preparing (recovering) purified 1,3-butadiene by a distillation process including extractive distillation from a C_4 hydrocarbon fraction containing 1,3-butadiene, may be mentioned a process illustrated in Fig. 1. However, for example, reboilers, condensers, heat exchangers, coolers, pumps, circulating circuits in respective distillation columns, and the like are omitted in Fig. 1 for the sake of brief description of the whole distillation process.

[0033] As illustrated in Fig. 1, a gasified C_4 hydrocarbon fraction is fed to a middle stage of a first extractive distillation column A through a pipe 21, while an extraction solvent such as N,N-dimethylformamide is fed thereto through a pipe 45 to conduct first-stage extractive distillation. In the first-stage extractive distillation, a raffinate composed of hydrocarbons (propane, propylene, isobutene, allene, n-butane, isobutene, 1-butene, trans-2-butene, cis-2-butene, etc.) lower in solubility in the extraction solvent than 1,3-butadiene is removed from the top of the column through a pipe 22. The main component of the raffinate is butene. However, the gas discharged from the top of the column is condensed by a condenser though not illustrated, and a part of the condensate is returned to the top of the column by refluxing. The pressure within the first distillation column is generally 1 to 15 atm, and the temperature at the bottom of the column is generally 100 to 180°C. The number of plates in the extractive distillation column may be suitably preset and is generally 100 to 300 plates and often about 200 plates in the case where the C_4 hydrocarbon fraction is used.

[0034] An extract containing 1,3-butadiene and hydrocarbons (methylacetylene, 1,2-butadiene, vinylacetylene, etc.) higher in solubility in the extraction solvent than 1,3-butadiene is taken out of the bottom of the first distillation column A and fed to an upper part of a preliminary stripping column B through a pipe 23. In the preliminary stripping column B, the hydrocarbons are partially stripped from the solvent and directly sent to a second distillation column E through a pipe 24. The bottoms in the preliminary stripping column B are fed to the top of a first stripping column C through a pipe 25, and the hydrocarbons are stripped from the solvent. The solvent discharged from the bottom of the first stripping column is cooled in a heat exchanger and circulated into the first extractive distillation column A. A hydrocarbon vapor discharged from the top of the first stripping column is introduced into a compressor D through pipes 26 and 27, compressed there and then fed to the bottom of a second extractive distillation column E through a pipe 28. The

preliminary stripping column B and first stripping column C can be operated under conditions that the pressure within each column is generally 1 to 2 atm, and the temperature at the bottom thereof is the boiling point of the solvent at the pressure thereof.

[0035] 1,3-Butadiene and hydrocarbons higher in solubility in the extraction solvent than 1,3-butadiene are mainly fed to the second extractive distillation column E. An extraction solvent is fed to a position lower by some plates than the top of the second extractive distillation column E through a pipe 37. A vapor discharged from the top of the second extractive distillation column is 1,3-butadiene containing a trace amount of impurities and refluxed by a condenser, and the remaining portion thereof is sent to a first fractional distillation column H through a pipe 29. A liquid composed mainly of the solvent at the bottom of the second extractive distillation column E is first fed to a butadiene recovering column F through a pipe 33 and then to a second stripping column G through a pipe 34, and the remaining hydrocarbons are stripped from the solvent there. The solvent discharged from the bottom of the second stripping column G is cooled by heat exchange and returned to the first extractive distillation column A and second extractive distillation column E through a pipe 36. A vapor at the top of the second stripping column G is refluxed by a condenser, and a gas remaining without being refluxed is discharged into a fuel gas system through a pipe 35. The operating conditions of the second extractive distillation column and second stripping column are the same as those of the first extractive distillation column and first stripping column, respectively.

[0036] Since a small amount of impurities still remain in a 1,3-butadiene fraction even by the two-stage extractive distillation, these impurities are removed by fractional distillation. In the first fractional distillation column H, impurities having a boiling point lower than that of 1,3-butadiene are removed. A vapor at the top of the first fractional distillation column H is partially condensed and refluxed, and the remainder is sent to the fuel gas system. The bottoms in the first fractional distillation column H are sent to a second fractional distillation column I though a pipe 30. A distillate from the second fractional distillation column I is provided as a 1,3-butadiene product through a pipe 31. The bottoms in the second fractional distillation column I are discharged as a waste liquid. The operating conditions of the respective fractional distillation columns are such that the pressure within each column is generally 1 to 15 atm, and the temperature within the column is the boiling point of the intended product at the pressure thereof. The number of plates in each distillation column may be suitably preset and is generally 50 to 200 plates and often about 100 plates in the case where the C_4 hydrocarbon fraction is used.

[0037] The extraction solvent is sent to a solvent-purifying column J, and the solvent purified by washing with water is returned to the extractive distillation columns though a pipe 44. Water and a waste liquid are discharged through a pipe 40 and out of a pipe 41 for water and out of a pipe 43 for the waste liquid.

[0038] In order to isolating and recovering a conjugated diene from the C_5 hydrocarbon fraction and C_4 hydrocarbon fraction, as described above, there is adopted a distillation process in which ① a two-stage extractive distillation step with the object of removing hardly soluble hydrocarbons and easily soluble hydrocarbons and ② a fractional distillation step of generally two stages making good use of a difference between boiling points, which is conducted between the extractive distillation steps of two stages or as a final step, are suitably combined with each other.

[0039] As the extraction solvent, is used any of various solvents which can dissolve and extract conjugated dienes and generally used in a technical field relating to extractive distillation, such as amide compounds, N-methylpyrrolidone, acetonitrile and N-formylmorpholine. Among these extraction solvents, amide compounds are preferred. As examples of the amide compounds, may be mentioned formamide, N,N-dimethylformamide, acetamide, N-ethylacetamide, N,N-dimethylacetamide, N-chloroacetamide, N-bromoacetamide, diacetamide, triacetamide, propionamide, butylamide, isobutylamide, valeramide, isovaleramide. hexanamide, heptanamide, octanamide, decanamide, acrylamide, chloroacetamide, dichloroacetamide, trichloroacetamide, glycol amide, lactamide, pyruvoamide, cyanoacetamide, 2-cyano-2-nitroacetamide, oxamide, malonamide, succinamide, adipamide, malamide, d-tartramide and N,N-dimethylacetoacetic acid amide. Among these, N,N-dimethylformamide (DMF) is particularly preferred.

[0040] Examples of extraction solvents other than those described above include acetone, methyl ethyl ketone, dioxane, isoprene cyclic sulfone, acetonitrile, alcohol, glycol, N-methylolamine, N-ethylsuccinimide, N-methylpyrrolidone, hydroxyethylpyrrolidone, N-methyl-5-methylpyrrolidone, 2-heptenone, morpholine, N-formylmorpholine, N-methylmorpholin-3-on, sulfolane, methylcarbitol, tetrahydrofuran, aniline, N-methyloxazolidone, N-methylimidazole, N,N'-dimethylimidazolin-2-on, methyl cyanoacetate, ethyl acetoacetate, ethyl acetate, dimethyl malonate, propylene carbonate, methylcarbitol, diethylene glycol monomethyl ether, dimethyl sulfoxide and γ-butyrolactone.

[0041] A proportion of the extraction solvent used is generally 100 to 1,000 parts by weight, preferably 200 to 800 parts by weight per 100 parts by weight of the conjugated diene-containing hydrocarbon mixture. The extraction solvent is fed into each extractive distillation column from a position higher than a position in the column to which the hydrocarbon mixture is fed. 4. Polymerization inhibitor:

[0042] In the present invention, a polymerization inhibitor composed of a combination of at least one compound (a) selected from the group consisting of a compound having an NO radical in its molecule and a precursor compound capable of forming an NO radical, and a phosphorus-containing compound (b) is used as a polymerization inhibitor for conjugated dienes.

[0084] The polymerization inhibitor according to the present invention may also be used by adding it to a monomer such as a conjugated diene, aromatic vinyl, ethylenically unsaturated nitrile or α-olefin, or a mixture of the monomers. Even in this case, a proportion of the polymerization inhibitor used is generally selected from a range of 0.1 to 2,000 ppm based on the weight of the monomer or the mixture of the monomers.

[0085] Other polymerization inhibitors, chain transfer agents, oxygen scavengers and the like may be used upon the use of the polymerization inhibitor according to the present invention within limits not impeding the objects of the present invention. The polymerization inhibitor according to the present invention may be used by mixing both components. However, both components may be separately added into such various systems as described above.

EXAMPLES

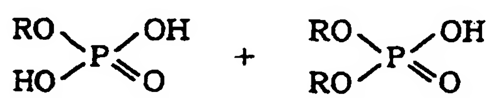
[0086] The present invention will hereinafter be described more specifically by the following Examples and Comparative Examples.

[Example 1]

[0087] A flow from the bottom of a first extractive distillation column, which had been obtained by subjecting a C_5 hydrocarbon fraction to extractive distillation with DMF in the first distillation column, i.e., an extract (more soluble extract) containing isoprene and substances (easily soluble hydrocarbons) higher in solubility in the solvent than isoprene, was used as "a conjugated-diene containing hydrocarbon mixture" to conduct the following experiment. The concentration of isoprene in the extract is about 15 wt.%.

[0088] A 100-ml pressure glass container was charged with 20 g of the extract. 180 ppm in total of oxygen (added 3 times in an amount of 60 ppm every 8 hours), iron pieces (used for evaluating corrosive property) and a polymerization inhibitor and closed to conduct a reaction at 125°C for 24 hours.

[0089] With respect to the polymerization inhibitor, N,N-diethylhydroxylamine (DEHA) was used as the compound (a). As the phosphorus-containing compound, was used a phosphate mixture (Ratemul P-909, product of Kao Corporation) represented by the formula (20):



(20)

$$R : C_9H_{19}-C_6H_4-O-(C_2H_4O)_8-C_2H_4-$$

which is a phosphate type surfactant (rust preventive). The respective components of the polymerization inhibitor were added 3 times each in an amount of 480 ppm every 8 hours.

[0090] After the reaction, the contents were filtered through filter paper, and a product obtained by drying solids remaining on the filter paper was regarded as "Polymer", while residue obtained by drying a filtrate was regarded as "High Boil". Both products are polymers formed by polymerization of isoprene, and "High Boil" is comparatively low in polymerization degree and hence corresponds to a rubbery polymer. The amounts of Polymer and High Boil were measured to calculate out their weight proportions (wt.%) to the amount of isoprene. On the other hand, change in the iron pieces was observed to evaluate the degree of corrosion. The unit is mg/dm^2 • day (weight loss, mg on corrosion for a day per 100 cm^2). The results are shown in Table 1.

[Comparative Examples 1 to 4]

[0091] Respective reactions were conducted in the same manner as in Example 1 except that the polymerization inhibitor was changed to their corresponding kinds and amounts added shown in Table 1. However, in Comparative Example 2, 2.5% furfural was first added. In Comparative Examples 3 and 4, the respective components were added 3 times each in an amount of 480 ppm every 8 hours. The results are shown in Table 1.

Table 1

	Polymerization inhibitor	Polymer (%)	High Boil (%)	Total (%)	Corrosion ($mg/dm^2 \cdot day$)
Ex. 1	DEHA/phosphorus-containing compound (each 480 ppm/time)	0.07	0.25	0.32	0.0
Comp. Ex. 1	Not added	1.00	0.08	1.08	1.5
Comp. Ex. 2	Furfural (2.5%/system)	0.32	0.16	0.48	3.0
Comp. Ex. 3	DEHA (480 ppm/time)	0.70	0.11	0.81	0.0
Comp. Ex. 4	DEHA/oxalic acid (1:2 mol) (480 ppm/time)	0.06	0.27	0.33	25.5

(Note)
(1) A DMF solution of crude isoprene (more soluble extract) was used.
(2) Oxygen = 60 ppm.
(3) Reaction conditions = 125°C x 24 hours.
(4) DEHA: N,N-diethylhydroxylamine.

[0092] As apparent from the results shown in Table 1, the polymerization reaction of isoprene is inhibited, and moreover no corrosion is caused when the polymerization inhibitor according to the present invention is used (Example 1). On the other hand, when no polymerization inhibitor is added (Comparative Example 1), the formation of a polymer is marked. When furfural proposed in the prior art was used (Comparative Example 2), the inhibitory effect on polymerization reaction was little, and corrosive property was recognized though it was extremely slight. When DEHA is used by itself (Comparative Example 3), the inhibitory effect on polymerization reaction is insufficient. When DEHA and oxalic acid are used in combination (Comparative Example 4), the inhibitory effect on polymerization reaction is good, but corrosive property is recognized, so that it is expected to form a popcorn polymer due to iron rust.

[Examples 2 to 5, and Comparative Examples 5 to 20]

[0093] Respective experiments were conducted in the same manner as in Example 1 except that ① a DMF solution of purified isoprene (isoprene concentration = 15 wt.%) was used in place of the DMF solution of crude isoprene, ② no iron piece was added, ③ the polymerization inhibitor was changed to their corresponding kinds and quantity proportions shown in Table 2, ④ the concentration of oxygen was changed from 60 ppm to 180 ppm, and ⑤ the reaction conditions were changed from 125°C for 24 hours to 100°C for 3 days. However, the respective components were first added to the system in their corresponding amounts shown in Table 2. Incidentally, in Comparative Example 5, neither oxygen nor polymerization inhibitor was added. In other Examples and Comparative Examples, oxygen was added in an amount of 180 ppm. The results are shown in Table 2.

Table 2

	Polymerization inhibitor	Polymer (%)	High Boil (%)	Total (%)
Ex. 2	DEHA (180 ppm)/phosphoric acid (180 ppm)	0.04	0.06	0.10
Ex. 3	DEHA (360 ppm)/phosphoric acid (180 ppm)	0.01	0.08	0.09
Ex. 4	DEHA (180 ppm)/Na dihydrogenphosphate (180 ppm)	0.01	0.06	0.07
Ex. 5	DEHA (360 ppm)/Na dihydrogenphosphate (180 ppm)	0.01	0.06	0.07
Comp. Ex. 5	Not added (oxygen was also not added)	0.06	0.12	0.18

Table 2 (continued)

	Polymerization inhibitor	Polymer (%)	High Boil (%)	Total (%)
Comp. Ex. 6	Only oxygen (180 ppm) was added	0.54	0.08	0.62
Comp. Ex. 7	Furfural (2.5%)	0.26	0.12	0.38
Comp. Ex. 8	DEHA (180 ppm)	0.19	0.09	0.28
Comp. Ex. 9	Phosphoric acid (180 ppm)	0.41	0.07	0.48
Comp. Ex. 10	Phosphoric acid (360 ppm)	0.26	0.08	0.34
Comp. Ex. 11	Na dihydrogenphosphate (180 ppm)	0.09	0.32	0.41
Comp. Ex. 12	Na dihydrogenphosphate (360 ppm)	0.13	0.28	041
Comp. Ex. 13	Hydroquinone (180 ppm)	0.41	0.48	0.89
Comp. Ex. 14	TBC (180 ppm)	0.04	0.31	0.35
Comp. Ex. 15	BHT (180 ppm)	0.61	0.10	0.71
Comp. Ex. 16	Monoethanolamine (180 ppm)	0.38	0.40	0.78
Comp. Ex. 17	Hydroquinone (180 ppm)/phosphoric acid (180 ppm)	0.34	0.11	0.45
Comp. Ex. 18	TBC (180 ppm)/phosphoric acid (180 ppm)	0.18	0.06	0.24
Comp. Ex. 19	BHT (180 ppm)/phosphoric acid (180 ppm)	0.35	0.07	0.42
Comp. Ex. 20	Monoethanolamine (180 ppm)/phosphoric acid (180 ppm)	0.38	0.10	0.48
(Note) (1) A DMF solution of purified isoprene was used. (2) Oxygen = 180 ppm. (3) Reaction conditions = 100°C x 3 days. (4) DEHA: N,N-diethylhydroxylamine. (5) TBC: 4-t-butylcatechol. (6) BHT: 2,6-di-t-butyl-4-methylphenol.				

[0094] As apparent from the results shown in Table 2, it is understood that when the polymerization inhibitors according to the present invention are used (Examples 2 to 5), the polymerization reaction is markedly inhibited. On the other hand, when no polymerization inhibitor is used (Comparative Examples 5 and 6), or the conventional polymerization inhibitors or polymerization inhibitors having a composition outside the range according to the present invention are used (Comparative Examples 7 to 20), no sufficient inhibitory effect on polymerization reaction cannot be achieved. Accordingly, it can be understood that when the method according to the present invention is applied to an actual distillation process including extractive distillation, an excellent inhibitory effect on the formation of a popcorn polymer and a rubbery polymer is brought about.

[Example 6]

[0095] Twenty grams of a dimethylformamide (DMF) solution (isoprene concentration = 15 wt.%) of purified isoprene (purity: 99.3%) were placed in a 100-ml pressure glass container, and 180 ppm in total of oxygen (added 3 times in an amount of 60 ppm every 8 hours), 90 ppm of sodium nitrite and 90 ppm of sodium dihydrogenphosphate were charged therein. After the container was closed, a reaction was conducted at 100°C for 3 days. Oxygen is added for the purpose of accelerating the reaction. After the reaction, the proportions of Polymer and High Boil formed were calculated out. The results are shown in Table 3.

[Examples 7 and Comparative Examples 21 to 24]

[0096] The same procedure as in Example 6 was followed except that the kind and amount added of the polymer-

ization inhibitor were respectively changed as shown in Table 3. However, in Comparative Example 21, no polymerization inhibitor was added, but only oxygen was added. In Comparative Examples 22 to 24 and Example 7, 180 ppm of oxygen were also added in the same manner as in Example 6. The results are shown in Table 3.

Table 3

	Polymerization inhibitor	Polymer (%)	High Boil (%)	Total (%)
Comp. Ex. 21	Oxygen (180 ppm)	0.46	0.21	0.67
Comp. Ex. 22	Na dihydrogenphosphate (180 ppm)	0.03	0.27	0.30
Comp. Ex. 23	Na nitrite (90 ppm)	0.02	0.14	0.16
Comp. Ex. 24	Na nitrite (180 ppm)	0.02	0.12	0.14
Ex. 6	Na nitrite (90 ppm)/Na dihydrogenphosphate (90 ppm)	0.01	0.06	0.07
Ex. 7	Na nitrite (180 ppm)/Na dihydrogenphosphate (180 ppm)	0.01	0.06	0.07

[0097] As apparent from the results shown in Table 3, it is understood that when the compound (a) and the phosphorus-containing compound (b) were used in combination as a polymerization inhibitor (Examples 6 and 7), the polymerization of isoprene was markedly inhibited compared with the results of Comparative Examples 21 to 24.

[Example 8]

[0098] Twenty grams of a DMF solution (butadiene concentration = 15 wt.%) of purified butadiene (purity: 99.2%) were placed in a 100-ml pressure glass container, and 180 ppm in total of oxygen (added 3 times in an amount of 60 ppm every 8 hours), 120 ppm of sodium nitrite and 120 ppm of sodium dihydrogenphosphate were charged therein. After the container was closed, a reaction was conducted at 100°C for 3 days. After the reaction, the amounts of Polymer and High Boil formed were measured in the same manner as in Example 1 to calculate out their proportions (wt.%) to the amount of butadiene. The results are shown in Table 4.

[Comparative Examples 25 and 26]

[0099] The same procedure as in Example 8 was followed except that the kind and amount added of the polymerization inhibitor were respectively changed as shown in Table 4. However, in Comparative Example 25, no polymerization inhibitor was added, but only oxygen was added. In Comparative Example 26, 180 ppm of oxygen were also added in the same manner as in Example 8. The results are shown in Table 4.

Table 4

	Polymerization inhibitor	Polymer (%)	High Boil (%)	Total (%)
Comp. Ex. 25	Oxygen (180 ppm)	0.29	0.08	0.37
Comp. Ex. 26	Na nitrite (120 ppm)	0.05	0.12	0.17
Ex. 8	Na nitrite (120 ppm)/Na dihydrogenphosphate (120 ppm)	0.01	0.08	0.09

[0100] As apparent from the results shown in Table 4, it is understood that when the compound (a) and the phosphorus-containing compound (b) were used in combination as a polymerization inhibitor (Example 8), the polymerization of butadiene was markedly inhibited compared with the results of Comparative Examples 25 to 26.

[Example 9]

[0101] Twenty grams of a DMF solution (butadiene concentration = 15 wt.%) of purified butadiene (purity: 99.2%) were placed in a 100-ml pressure glass container, and 180 ppm in total of oxygen (added 3 times in an amount of 60

ppm every 8 hours), 90 ppm of sodium nitrite and 90 ppm of sodium dihydrogenphosphate were charged therein. After the container was closed, a reaction was conducted at 100°C for 3 days. After the reaction, the proportions of Polymer and High Boil formed were calculated out. The results are shown in Table 5.

[Comparative Examples 27 and 28]

[0102] The same procedure as in Example 9 was followed except that the kind and amount added of the polymerization inhibitor were respectively changed as shown in Table 5. However, in Comparative Example 27, no polymerization inhibitor was added, but only oxygen was added. In Comparative Example 28, 180 ppm of oxygen were also added in the same manner as in Example 9. The results are shown in Table 4.

Table 5

	Polymerization inhibitor	Polymer (%)	High Boil (%)	Total (%)
Comp. Ex. 27	Oxygen (180 ppm)	0.29	0.06	0.35
Comp. Ex. 28	Na nitrite (90 ppm)	0.04	0.09	0.13
Ex. 9	Na nitrite (90 ppm)/Na dihydrogenphosphate (90 ppm)	0.01	0.05	0.06

[0103] As apparent from the results shown in Table 5, it is understood that when the compound (a) and the phosphorus-containing compound (b) were used in combination as a polymerization inhibitor (Example 8), the polymerization of butadiene was markedly inhibited compared with the results of Comparative Examples 27 to 28 even when the amounts of these compounds added were small.

[Example 10]

[0104] Twenty grams of a DMF solution (isoprene concentration = 15 wt.%) of purified isoprene were placed in a 100-ml pressure glass container, and 180 ppm in total of oxygen (added 3 times in an amount of 60 ppm every 8 hours), 180 ppm of 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl and 180 ppm of sodium dihydrogenphosphate were charged therein. After the container was closed, a reaction was conducted at 100°C for 3 days. After the reaction, the proportions of Polymer and High Boil formed were calculated out. The results are shown in Table 6.

[Example 11 and Comparative Examples 29 to 32]

[0105] The same procedure as in Example 10 was followed except that the kind and amount added of the polymerization inhibitor were respectively changed as shown in Table 6. However, in Comparative Example 29, no polymerization inhibitor was added, but only oxygen was added. In Comparative Examples 30 to 32 and Example 11, 180 ppm of oxygen were also added in the same manner as in Example 10. The results are shown in Table 6.

Table 6

	Polymerization inhibitor	Polymer (%)	High Boil (%)	Total (%)
Comp. Ex. 29	Oxygen (180 ppm)	0.39	0.19	0.58
Comp. Ex. 30	Na dihydrogenphosphate (180 ppm)	0.02	0.29	0.31
Comp. Ex. 31	4-Oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (180 ppm)	0.37	0.06	0.43
Comp. Ex. 32	4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (180 ppm)	0.22	0.06	0.28
Ex. 10	4-Oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (180 ppm)/Na dihydrogenphosphate (180 ppm)	0.02	0.06	0.08
Ex. 11	4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (180 ppm)/Na dihydrogenphosphate (180 ppm)	0.01	0.05	0.06

[0106] As apparent from the results shown in Table 6, it is understood that when the compound (a) and the phosphorus-containing compound (b) were used in combination as a polymerization inhibitor (Examples 10 and 11), the polymerization of isoprene was markedly inhibited compared with the results of Comparative Examples 29 to 32.

[Example 12]

[0107] Twenty grams of a DMF solution (isoprene concentration = 15 wt.%) of purified isoprene were placed in a 100-ml pressure glass container, and 180 ppm in total of oxygen (added 3 times in an amount of 60 ppm every 8 hours), 180 ppm of nitrosophenylhydroxyamine ammonium salt and 180 ppm of sodium dihydrogenphosphate were charged therein. After the container was closed, a reaction was conducted at 100°C for 3 days. After the reaction, the proportions of Polymer and High Boil formed were calculated out in the same manner as in Example 1. The results are shown in Table 7.

[Comparative Examples 33 and 35]

[0108] The same procedure as in Example 12 was followed except that the kind and amount added of the polymerization inhibitor were respectively changed as shown in Table 7. However, in Comparative Example 33, no polymerization inhibitor was added, but only oxygen was added. In Comparative Examples 34 and 35, 180 ppm of oxygen were also added in the same manner as in Example 12. The results are shown in Table 7.

Table 7

	Polymerization inhibitor	Polymer (%)	High Boil (%)	Total (%)
Comp. Ex. 33	Oxygen (180 ppm)	0.22	0.06	0.28
Comp. Ex. 34	Na dihydrogenphosphate (180 ppm)	0.13	0.24	0.37
Comp. Ex. 35	Nitrosophenylhydroxyamine ammonium salt (180 ppm)	0.26	0.07	0.33
Ex. 12	Nitrosophenylhydroxyamine ammonium salt (180 ppm)/Na dihydrogenphosphate (180 ppm)	0.09	0.05	0.14

[0109] As apparent from the results shown in Table 7, it is understood that when the compound (a) and the phosphorus-containing compound (b) were used in combination as a polymerization inhibitor (Example 12), the polymerization of isoprene was markedly inhibited compared with the results of Comparative Examples 33 to 35.

[Example 13]

[0110] Twenty grams of a DMF solution (isoprene concentration = 15 wt.%) of purified isoprene were placed in a 100-ml pressure glass container, and 180 ppm in total of oxygen (added 3 times in an amount of 60 ppm every 8 hours), 180 ppm of sodium nitrite and 180 ppm of sodium dihydrogenphosphate were charged therein. After the container was closed, a reaction was conducted at 100°C for 3 days.

[0111] After the reaction, the proportions of Polymer and High Boil formed were calculated out in the same manner as in Example 1. The results are shown in Table 8.

[Example 14]

[0112] The experiment was conducted in the same manner as in Example 13 except that Perex RP (sesquipolyethylene-2-ethylhexyl phosphate) produced by Kao Corporation was used in place of sodium dihydrogenphosphate. The results are shown in Table 8.

[Example 15]

[0113] The experiment was conducted in the same manner as in Example 13 except that tris(nonylphenyl)phosphite was used in place of sodium dihydrogenphosphate. The results are shown in Table 8.

[Comparative Example 36]

[0114] The experiment was conducted in the same manner as in Example 13 except that no polymerization inhibitor was added, but only oxygen was added. The results are shown in Table 8.

[Comparative Example 37]

[0115] The experiment was conducted in the same manner as in Example 13 except that 180 ppm of sodium nitrite were added as a polymerization inhibitor. The results are shown in Table 8.

Table 8

	Polymerization inhibitor	Polymer (%)	High Boil (%)	Total (%)
Comp. Ex. 36	Oxygen (180 ppm)	0.41	0.08	0.49
Comp. Ex. 37	Na nitrite (180 ppm)	0.03	0.13	0.16
Ex. 13	Na nitrite (180 ppm)/Na dihydrogenphosphate (180 ppm)	0.01	0.05	0.06
Ex. 14	Na nitrite (180 ppm)/ Perex RP (180 ppm)	0	0.06	0.06
Ex. 15	Na nitrite (180 ppm)/tris-(nonylphenyl)phosphite (180 ppm)	0.01	0.07	0.08

[0116] As apparent from the results shown in Table 8, it is understood that when the compound (a) and the phosphorus-containing compound (b) were used in combination as a polymerization inhibitor (Examples 13 to 15), the polymerization of isoprene was markedly inhibited compared with the results of Comparative Examples 36 and 37.

[Example 16]

[0117] Twenty grams of a DMF solution (isoprene concentration = 15 wt.%) of purified isoprene were placed in a 100-ml pressure glass container, and 180 ppm in total of oxygen (added 3 times in an amount of 60 ppm every 8 hours), 180 ppm of N,N-dimethylhydroxylamine (DEHA), 3.6 ppm of sodium dihydrogenphosphate and iron pieces were charged therein. After the container was closed, a reaction was conducted at 100°C for 3 days. After the reaction, the proportions of Polymer and High Boil formed were calculated out in the same manner as in Example 1. The results are shown in Table 9.

[Examples 17 to 21, and Comparative Examples 38 to 46]

[0118] The reaction was conducted in the same manner as in Example 16 except that the polymerization inhibitor was changed to their corresponding kinds and amounts added shown in Table 9. The results are shown in Table 9.

Table 9

	Oxygen (ppm)	DEHA (ppm)	Phosphorus-containing compound		Polymer (%)	High Boil (%)	Total (%)
			Kind	(ppm)			
Comp. Ex. 38	-	-	Not added	-	0.09	0.08	0.17
Comp. Ex. 39	180	-	Not added	-	0.58	0.08	0.66
Comp. Ex. 40	180	180	Not added	-	0.27	0.06	0.33

Table 9 (continued)

	Oxygen (ppm)	DEHA (ppm)	Phosphorus-containing compound		Polymer (%)	High Boil (%)	Total (%)
			Kind	(ppm)			
Comp. Ex. 41	180	-	Na dihydrogenphosphate	180	0.05	0.23	0.28
Comp. Ex. 42	180	-	Hexamethylphosphorus triamide	180	0.12	0.07	0.19
Comp. Ex. 43	180	-	Triphenylphosphine	180	0.20	0.36	0.56
Comp. Ex. 44	180	-	Trimiethyl phosphonate	180	0.08	0.28	0.36
Comp. Ex. 45	180	-	Triphenyl phosphonate	180	0.48	0.09	0.57
Comp. Ex. 46	180	-	Triethylphosphine	180	0.27	0.25	0.52
Ex. 16	180	180	Na dihydrogenphosphate	3.6	0.02	0.06	0.08
Ex. 17	180	180	Hexamethylphosphorus triamide	18	0.04	0.04	0.08
Ex. 18	180	180	Triphenylphosphine	18	0.02	0.07	0.09
Ex. 19	180	180	Trimethyl phosphonate	18	0.06	0.04	0.10
Ex. 20	180	180	Triphenyl phosphonate	18	0.05	0.09	0.14
Ex. 21	180	180	Triethylphosphine	18	0.05	0.10	0.15

(Note)
(1) DEHA: N,N-diethylhydroxylamine.

[0119] As apparent from the results shown in Table 9, it is understood that when the compound (a) and the phosphorus-containing compound (b) were used in combination as a polymerization inhibitor (Examples 16 to 21), the polymerization of isoprene was markedly inhibited compared with the results of Comparative Examples 38 to 46. In addition, no corrosion of the iron pieces was observed in the respective Examples.

[Example 22]

[0120] Twenty grams of a DMF solution (isoprene concentration = 15 wt.%) of purified isoprene were placed in a 100-ml pressure glass container, and 180 ppm in total of oxygen (added 3 times in an amount of 60 ppm every 8 hours), 180 ppm of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (HTPO), 180 ppm of hexamethylphosphorus triamide and iron pieces were charged therein. After the container was closed, a reaction was conducted at 100°C for 3 days. After the reaction, the proportions of Polymer and High Boil formed were calculated out in the same manner as in Example

1. The results are shown in Table 10.

[Examples 23 to 25, and Comparative Examples 47 to 49]

[0121] The reaction was conducted in the same manner as in Example 22 except that the polymerization inhibitor was changed to their corresponding kinds and amounts added shown in Table 10. The results are shown in Table 10.

Table 10

	Oxygen (ppm)	HTPO (ppm)	Phosphorus-containing compound		Polymer (%)	High Boil (%)	Total (%)
			Kind	(ppm)			
Comp. Ex. 47	-	-	Not added	-	0.09	0.08	0.17
Comp. Ex. 48	180	-	Not added	-	0.57	0.08	0.65
Comp. Ex. 49	180	180	Not added	-	0.14	0.07	0.21
Ex. 22	180	180	Hexamethyl-phosphorus triamide	180	0.00	0.02	0.02
Ex. 23	180	180	Triethylphos-phine	180	0.01	0.04	0.05
Ex. 24	180	180	Triphenyl-phosphine	180	0.06	0.05	0.11
Ex. 25	180	180	Trimethyl phospho-nate	180	0.06	0.06	0.12

(Note)
(1) HTPO: 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl.

[0122] As apparent from the results shown in Table 10, it is understood that when the compound (a) and the phosphorus-containing compound (b) were used in combination as a polymerization inhibitor (Examples 22 to 25), the polymerization of isoprene was markedly inhibited compared with the results of Comparative Examples 47 to 49. In addition, no corrosion of the iron pieces was observed in the respective Examples.

[Example 26]

[0123] After 500 ml of styrene were washed twice with 200 ml of 1N caustic soda and then twice with 200 ml of water, zeolite (Zeolite A-3, product of Tosoh Corp.) was poured therein to dry styrene. In this example, the washing and drying were respectively conducted by shaking the mixture containing styrene and the like for 2 to 3 minutes in a bottle.

[0124] Styrene purified above was taken out and charged into an ampoule. At this time, 50 ppm of N,N-diethylhydroxylamine (DEHA) and 50 ppm of Na dihydrogenphosphate were added. An air atmosphere was used as an atmosphere. After a reaction was conducted at 120°C for 1 hour, the reaction mixture was dried to measure the amount of High Boil formed. The result is shown in Table 11.

[Examples 27 and 28, and Comparative Examples 50 to 53]

[0125] The reaction was conducted in the same manner as in Example 26 except that the polymerization inhibitor was changed to their corresponding kinds and amounts added shown in Table 11. The results are shown in Table 11.

Table 11

	NO radical compound or precursor		Na dihydrogenphosphate (ppm)	High Boil (%)
	Kind	(ppm)		
Comp. Ex. 50	Not added	-	0	10.40
Comp. Ex. 51	DEHA	50	0	5.71
Ex. 26	DEHA	50	50	1.79
Comp. Ex. 52	HTPO	50	0	0.44
Ex. 27	HTPO	50	50	0.17
Comp. Ex. 53	BOTS	50	0	3.34
Ex. 28	BOTS	50	50	2.33

(Note)
(1) DEHA: N,N-diethylhydroxylamine.
(2) HTPO: 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl.
(3) BOTS: bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

[0126] As apparent from the results shown in Table 11, it is understood that when the compound (a) and the phosphorus-containing compound (b) were used in combination as a polymerization inhibitor (Examples 26 to 28), the polymerization of styrene was markedly inhibited compared with the results of Comparative Examples 50 to 53.

[Examples 29 and 30, and Comparative Examples 54 and 55]

[0127] The experiment was conducted in the same manner as in Example 26 except that the proportions of the compound (a) and Na dihydrogenphosphate used were changed as shown in Table 12, and the reaction was conducted at 120°C for 3 hours. The results are shown in Table 12.

Table 12

	NO radical compound or precursor		Na dihydrogenphosphate (ppm)	High Boil (%)
	Kind	(ppm)		
Comp. Ex. 54	HTPO	500	0	1.63
Ex. 29	HTPO	500	500	0.31
Comp. Ex. 55	BOTS	500	0	2.54
Ex. 28	BOTS	500	500	0.40

(Note)
(1) HTPO: 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl.
(2) BOTS: bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

[0128] As apparent from the results shown in Table 12, it is understood that when the compound (a) and the phosphorus-containing compound (b) were used in combination as a polymerization inhibitor (Examples 29 and 30), the polymerization of styrene was markedly inhibited compared with the results of Comparative Examples 54 and 55.

INDUSTRIAL APPLICABILITY

[0129] According to the present invention, there are provided polymerization inhibitors, a polymerization-inhibiting method and polymerization-inhibiting compositions comprising a monomer and a polymerization inhibitor for inhibiting

the occurrence of unfavorable premature polymerization in various operating steps such as the production, purification, storage, shipment, preparation and use of a monomer such as a conjugated diene, aromatic vinyl, ethylenically unsaturated nitrile or α-olefin, a mixture of the monomers or a hydrocarbon mixture containing the monomer.

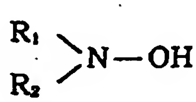
[0130] The polymerization inhibitors according to the present invention are particularly effective for inhibiting the formation of a popcorn polymer and a rubbery polymer in a production process of a purified conjugated diene, comprising isolating the conjugated diene by conducting a distillation process including extractive distillation from a conjugated diene-containing hydrocarbon mixture.

Claims

1. A polymerization-inhibiting composition comprising at least one compound (a) selected from the group consisting of a compound having an NO radical in its molecule and a precursor compound capable of forming an NO radical, a phosphorus-containing compound (b), and at least one monomer (c) selected from the group consisting of a conjugated diene, an aromatic vinyl, an ethylenically unsaturated nitrile and an α-olefin, wherein a weight ratio of the compound (a) to the phosphorus-containing compound (b) is 1:10 to 100:1.

2. The polymerization-inhibiting composition according to Claim 1, wherein the compound (a) is at least one compound selected from the group consisting of an N,N-dialkylhydroxylamine, a sterically hindered nitroxyl compound and a sterically hindered hydroxylamine compound.

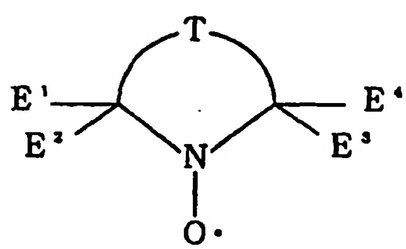
3. The polymerization-inhibiting composition according to Claim 2, wherein the N,N-dialkylhydroxylamine is a compound represented by the formula (I):



(I)

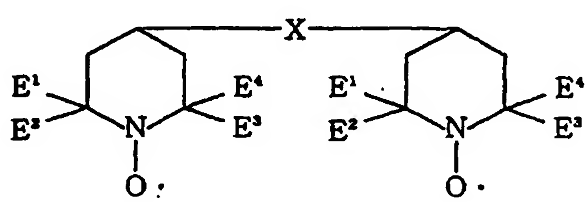
wherein R_1 and R_2 are independently a linear, branched or cyclic alkyl group having 1 to 10 carbon atoms.

4. The polymerization-inhibiting composition according to Claim 2, wherein the sterically hindered nitroxyl compound is a compound represented by the formula (II):



(II)

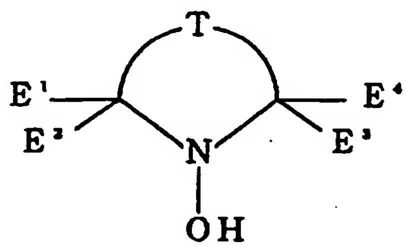
wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and T is an organic group required to form a 5- or 6-membered ring, or a compound represented by the formula (IV):



(IV)

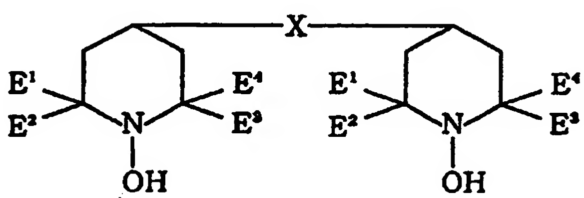
wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and X is a divalent linking group.

5. The polymerization-inhibiting composition according to Claim 2, wherein the sterically hindered hydroxylamine compound is a compound represented by the formula (III):



(III)

wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and T is an organic group required to form a 5- or 6-membered ring, or a compound represented by the formula (V):



(V)

wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and X is a divalent linking group.

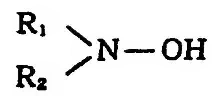
6. The polymerization-inhibiting composition according to Claim 1, wherein the phosphorus-containing compound (b) is at least one selected from the group consisting of phosphoric compounds, esterified products of the phosphoric compounds, alkali metal salts or ammonium salts of the phosphoric compounds, compounds obtained by introducing an ester linkage and an alkali metal salt linkage or an ammonium salt linkage into the phosphoric compounds, phosphine compounds, and hexaalkylphosphorus triamides.

7. The polymerization-inhibiting composition according to Claim 1, wherein the monomer (c) is a conjugated diene.

8. A polymerization inhibitor for at least one monomer (c) selected from the group consisting of a conjugated diene, an aromatic vinyl, an ethylenically unsaturated nitrile and an α-olefin, comprising at least one compound (a) selected from the group consisting of a compound having an NO radical in its molecule and a precursor compound capable of forming an NO radical, and a phosphorus-containing compound (b), wherein a weight ratio of the compound (a) to the phosphorus-containing compound (b) is 1:10 to 100:1.

9. The polymerization inhibitor according to Claim 8, wherein the compound (a) is at least one compound selected from the group consisting of an N,N-dialkylhydroxylamine, a sterically hindered nitroxyl compound and a sterically hindered hydroxylamine compound.

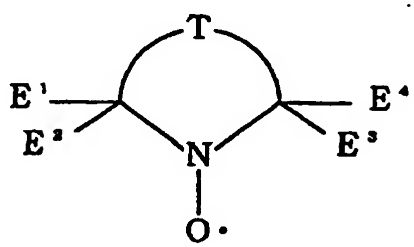
10. The polymerization inhibitor according to Claim 9, wherein the N,N-dialkylhydroxylamine is a compound represented by the formula (I):



(I)

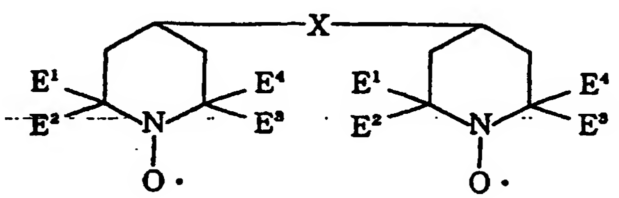
wherein R_1 and R_2 are independently a linear, branched or cyclic alkyl group having 1 to 10 carbon atoms.

11. The polymerization inhibitor according to Claim 9, wherein the sterically hindered nitroxyl compound is a compound represented by the formula (II):



(II)

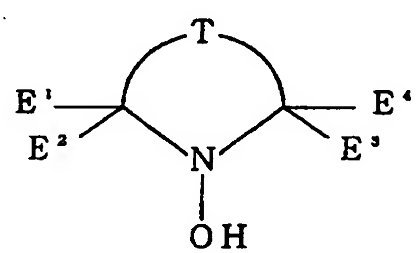
wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and T is an organic group required to form a 5- or 6-membered ring, or a compound represented by the formula (IV):



(IV)

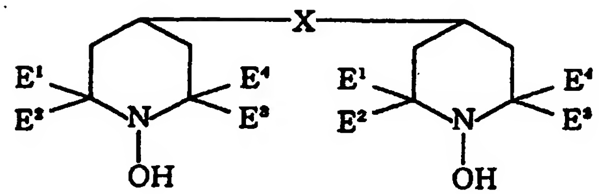
wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and X is a divalent linking group.

12. The polymerization inhibitor according to Claim 9, wherein the sterically hindered hydroxylamine compound is a compound represented by the formula (III):



(III)

wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and T is an organic group required to form a 5- or 6-membered ring, or a compound represented by the formula (V):



(V)

wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and X is a divalent linking group.

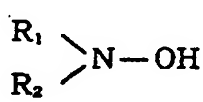
13. The polymerization inhibitor according to Claim 8, wherein the phosphorus-containing compound (b) is at least one selected from the group consisting of phosphoric compounds, esterified products of the phosphoric compounds, alkali metal salts or ammonium salts of the phosphoric compounds, compounds obtained by introducing an ester linkage and an alkali metal salt linkage or an ammonium salt linkage into the phosphoric compounds, phosphine compounds, and hexaalkylphosphorus triamides.

14. The polymerization inhibitor according to Claim 8, wherein the monomer (c) is a conjugated diene.

15. A method for inhibiting polymerization, which comprises causing at least one compound (a) selected from the group consisting of a compound having an NO radical in its molecule and a precursor compound capable of forming an NO radical, and a phosphorus-containing compound (b) to coexist at a weight ratio of the compound (a) to the phosphorus-containing compound (b) of 1:10 to 100:1 with at least one monomer (c) selected from the group consisting of a conjugated diene, an aromatic vinyl, an ethylenically unsaturated nitrile and an α-olefin.

16. The polymerization-inhibiting method according to Claim 15, wherein the compound (a) is at least one compound selected from the group consisting of an N,N-dialkylhydroxylamine, a sterically hindered nitroxyl compound and a sterically hindered hydroxylamine compound.

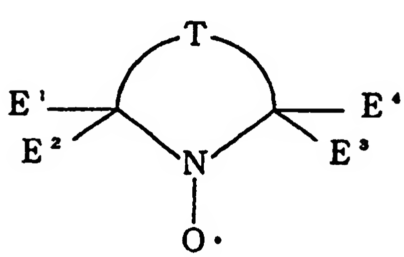
17. The polymerization-inhibiting method according to Claim 16, wherein the N,N-dialkylhydroxylamine is a compound represented by the formula (I):



(I)

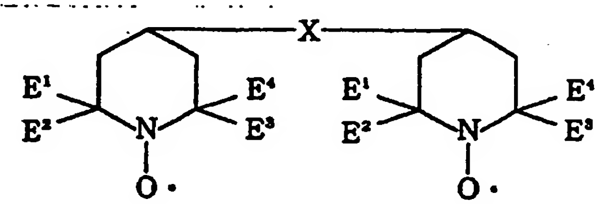
wherein R_1 and R_2 are independently a linear, branched or cyclic alkyl group having 1 to 10 carbon atoms.

18. The polymerization-inhibiting method according to Claim 16, wherein the sterically hindered nitroxyl compound is a compound represented by the formula (II):



(II)

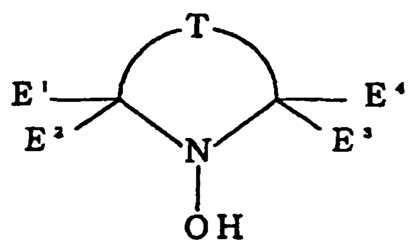
wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and T is an organic group required to form a 5- or 6-membered ring, or a compound represented by the formula (IV):



(IV)

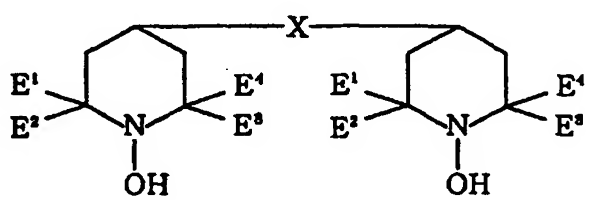
wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and X is a divalent linking group.

19. The polymerization-inhibiting method according to Claim 16, wherein the sterically hindered hydroxylamine compound is a compound represented by the formula (III):



(III)

wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and T is an organic group required to form a 5- or 6-membered ring, or a compound represented by the formula (V):



(V)

wherein the nitrogen atom is bonded directly to 2 tetrasubstituted carbon atoms, E_1, E_2, E_3 and E_4 are independently an organic group, and X is a divalent linking group.

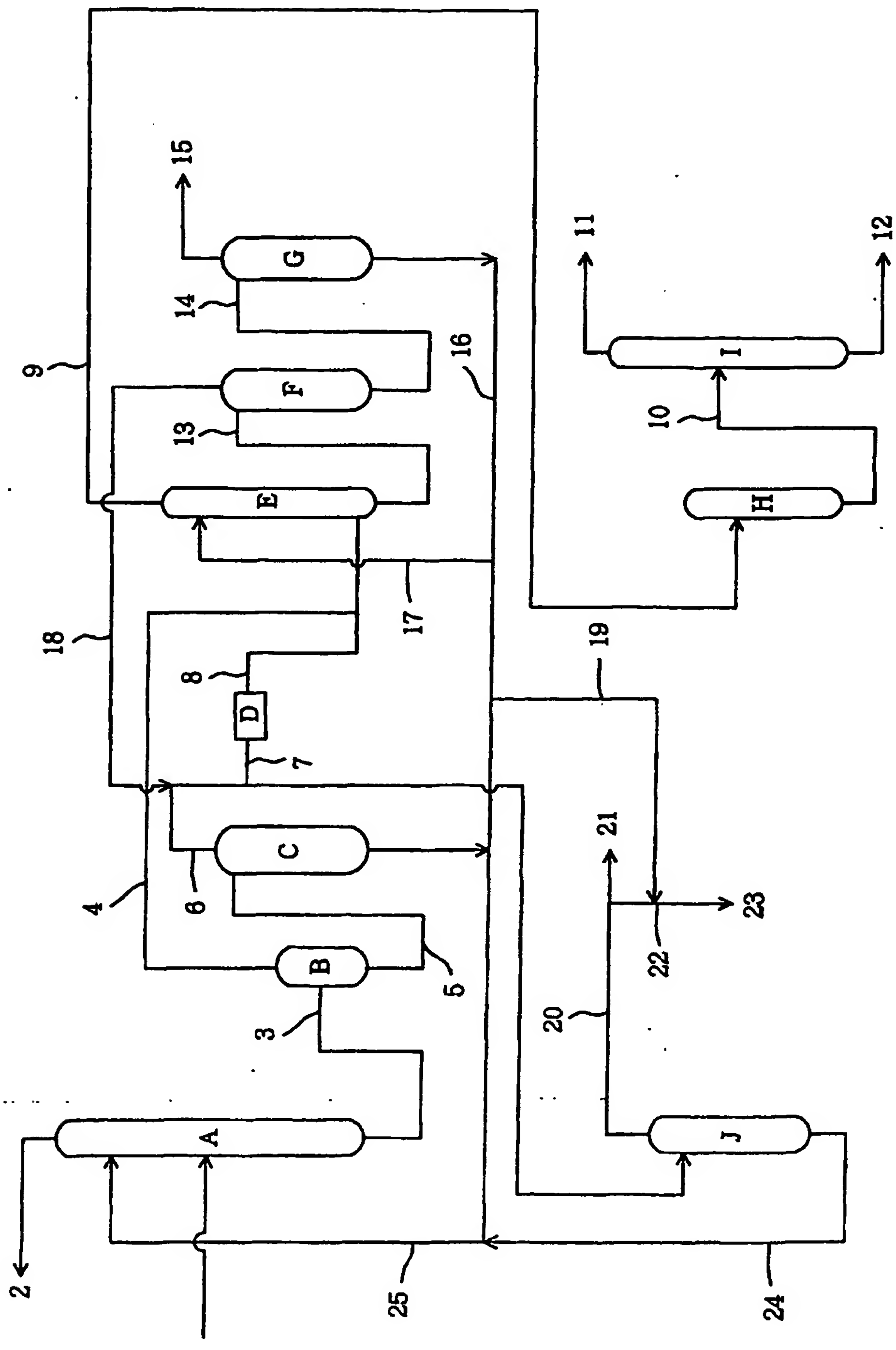
20. The polymerization-inhibiting method according to Claim 15, wherein the phosphorus-containing compound (b) is at least one selected from the group consisting of phosphoric compounds, esterified products of the phosphoric compounds, alkali metal salts or ammonium salts of the phosphoric compounds, compounds obtained by introducing an ester linkage and an alkali metal salt linkage or an ammonium salt linkage into the phosphoric compounds, phosphine compounds, and hexaalkylphosphorus triamides.

21. The polymerization-inhibiting method according to Claim 15, wherein the monomer (c) is a conjugated diene.

22. The polymerization-inhibiting method according to Claim 15, wherein the compound (a) and the phosphorus-containing compound (b) are caused to coexist with an conjugated diene in a preparation process of a purified conju-

gated diene, comprising isolating the conjugated diene by conducting a distillation process including extractive distillation from a conjugated diene-containing hydrocarbon mixture.

FIG. 1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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP99/01017

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[6] C07C11/18, 11/167, 239/08, 7/20, C07F9/09, 9/50, C08F2/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[6] C07C11/18, 11/167, 239/08, 7/20, C07F9/09, 9/50, C08F2/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 9-316026, A (Mitsubishi Chemical Corp.), 9 December, 1997 (09. 12. 97), Claims & EP, 810196, A1 & US, 5856562, A	1-22
A	JP, 5-202256, A (Japan Synthetic Rubber Co., Ltd.), 10 August, 1993 (10. 08. 93), Claims (Family: none)	1-22

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 May, 1999 (12. 05. 99)	25 May, 1999 (25. 05. 99)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

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